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INVESTIGATION OF SCHOTTKY BARRIERS

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This report summarizes the technical progress made in the past year under the auspices of AFOSR Contract F49620-86-K 0018. Substantial progress has been made in two key areas, in the study of perturbations to transport in Schottky barriers, and in development of *ab initio* electronic structure techniques tailored to the study of Schottky barriers.

The objective of the Schottky barrier transport studies is to obtain quantitative modeling of current transport through the depletion region that complements the experimental work of Professor Spicer at Stanford, and of the development of electronic structure techniques to provide a means to study the energetics of formation of Schottky barriers, and other properties related to electronic structure, such as band offsets and band structure. Both projects are heavily computational by nature, and this year's progress was mostly confined to developing the required numerical techniques that will yield the desired results. This report shows that substantial progress has been made in both areas, and that we are nearing completion of working tools that will enable to conduct new studies concerning several different aspects of Schottky barrier phenomena.

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I SCHOTTKY BARRIERS WORK

The Schottky barriers work concentrated this year on transport in the depletion region. *Transport* includes both the depletion region and the quasineutral region, and phenomena causing departures from ideal electrical behavior occurs in both. In last year's report, however, it was shown that the depletion region can and should be treated separately from the quasineutral region; the two can be coupled together by effective boundary conditions at the interface. What is required in the depletion region are the scattering probabilities (or equivalently the transmission and reflection coefficients) for an incident electron entering the depletion region. Last year's work centered on numerical solutions of the Boltzmann transport equations in the quasineutral region for a highly non-Boltzmann, spatially varying electron distribution subject to boundary conditions at the interface connecting the quasineutral and depletion regions. This year's work has focused on depletion region, to obtain the scattering rates of electrons traversing it. At this time last year, it was believed that scattering from a collection of random impurities (in contradistinction to a jellium of charge which gives rise to the usual one-dimensional quadratic potential barrier) would be very large (Boudville and McGill, 1985) and would require a fully three-dimensional solution the time-dependent Schrödinger equation for an (effective mass) electron moving through the depletion region. A careful study of the effect of a distribution of random impurities is discussed in the following pages. The barrier resulting from a distribution of random impurities was found—somewhat surprisingly—to differ remarkably little from that of a jellium. The difference between these potentials acts as a weak perturbation to electrons traversing the barrier.

This result greatly simplifies the calculation of scattering in the depletion region, because now coulomb scattering can possibly be neglected, or be treated in perturbation theory on the same footing as the other scattering mechanisms (e.g., intervalley scattering and optical phonon scattering). Electron scattering is dominated by a smooth one-dimensional potential, which includes the parabolic potential of jellium, the 1/z potential from image-force lowering, and possibly another short-range potential from metal-induced gap states or interfacial states.

We can exploit the smallness of the perturbation in the following way. The scattering rate w is given by Fermi's golden rule in terms of the T matrix (Schiff, 1968):

$$w = \frac{2\pi}{\hbar}\,\rho(\beta)\,|\langle\beta|T|\alpha\rangle|^2$$

where $\rho(\beta)$ is the density of outgoing states and the T matrix

$$|\langle\beta|T|\alpha\rangle| = \int u_\beta^*(\vec{r})V(\vec{r})\xi_\alpha(\vec{r})d^3r$$

represents the transmission amplitude coupling a free electron state u_β to a scattered outgoing state ξ_α. (ξ is a solution to the full Hamiltonian, including the potential V.)

By expressing the scattering potential as a sum of two terms V_1 and V_p, where V_1 is the large one-dimensional potential and V_p is the small perturbation, it turns out to be possible to express the T matrix as a sum of a part that arises from V_1 alone and a correction term (Schiff, 1968). The T matrix is given by

$$|\langle\beta|T|\alpha\rangle| = |\langle\beta|T_1|\alpha\rangle| + \int\xi_{1\beta}^*(\vec{r})V_p(\vec{r})\xi_\alpha(\vec{r})d^3r$$

$$\approx |\langle\beta|T_1|\alpha\rangle| + \int\xi_{1\beta}^*(\vec{r})V_p(\vec{r})\xi_{1\alpha}(\vec{r})d^3r$$

In the approximate expression, the second term contains a matrix element of V_p between states distorted by the V_1. This approximation consists in replacing in the second term the true scattered state by one distorted only by V_1. Because V_p is small, the approximation should be quite good, essentially exact for our purposes. Because V_1 is only one-dimensional, it is tractable to obtain the T matrix exactly for V_1, the resulting wave functions ξ can be used to obtain the second terms in the above expression and the total scattering rate can be evaluated.

To this end, we have developed a code that solves numerically the wave functions and T matrix for effective mass electrons in an arbitrary one-dimensional potential. There are some difficulties associated with numerical solutions, because the wave functions have a high kinetic energy in some regions that make the wave function oscillate rapidly. In tunneling regions, the wave functions are growing or decaying exponentially and the Schrödinger equation for those regions is of the stiff type. To obviate this difficulty, we divide space into three regions, the left side for which energy is greater than the potential, middle for which energy is less than the

potential and right for which energy is again greater. (For electrons with positive kinetic energy everywhere, there is no middle region.) With two linearly independent solutions in all three regions, a solution valid everywhere is obtained by matching the solution first at one turning point, then at the other. At the far edge of the left and right sides, the potential is assumed constant so that $\psi(z) = \exp(\pm ikz)$. For the propagating regions, the wave function is recast as amplitude and phase,

$$\psi(z) = R(z) \exp[\pm i\phi(z)]$$

and the Schrödinger equation becomes

$$R''(z) = [V_1(z) - E]R + E/R^3$$

$$\phi'(z) = \sqrt{E}/R^2 \quad .$$

In the tunneling regions, ψ is recast reflect its exponentially varying behavior:

$$\psi(z) = \exp[\phi(z)]$$

and the Schrödinger equation becomes:

$$\phi''(z) = -\phi'(z)^2 + V(z) - E \quad .$$

The two linearly independent solutions can be obtained by starting with any different set of initial conditions. In practice, the equation is integrated from the left to the right with one set of initial conditions and the right to the left with another; this avoids the problem of solving stiff equations. [It is also possible to solve the Schrödinger equation in a WKB approximation; however, for arbitrary potentials it is necessary to solve the equations numerically anyway, and the WKB may not be accurate near the surface where the potential varies rapidly: it is there that the image force lowering potential the MIGS potential (or whatever potential is responsible for pinning the Schottky barriers) are present.]

It is well known that electrons traversing the barrier can tunnel with kinetic energy less than the barrier height (the majority of current is tunneling current is moderately and heavily doped devices), and reflect off the barrier even with positive kinetic energy [see, for example, Landau and Liftshitz Section 50]. When calculating this effect in Schottky barriers, it has been

customary to approximate the potential barrier's shape either by a triangle or, for reflection over the top of the barrier, by a parabola. Our program permits us to calculate numerically the true reflection coefficient; it is found to differ significantly from the model potentials. Figure 1 compares the reflection for a potential obtained by a jellium with an image force superimposed to that with parabolic potential whose curvature matches the former potential. These differences are important when a quantitative comparison with experiment is desired. In cases when the band structure deviates significantly from effective mass behavior (this is especially important for tunneling electrons), one can easily include this effect using a two-band model or approximately by permitting the mass to be position-dependent.

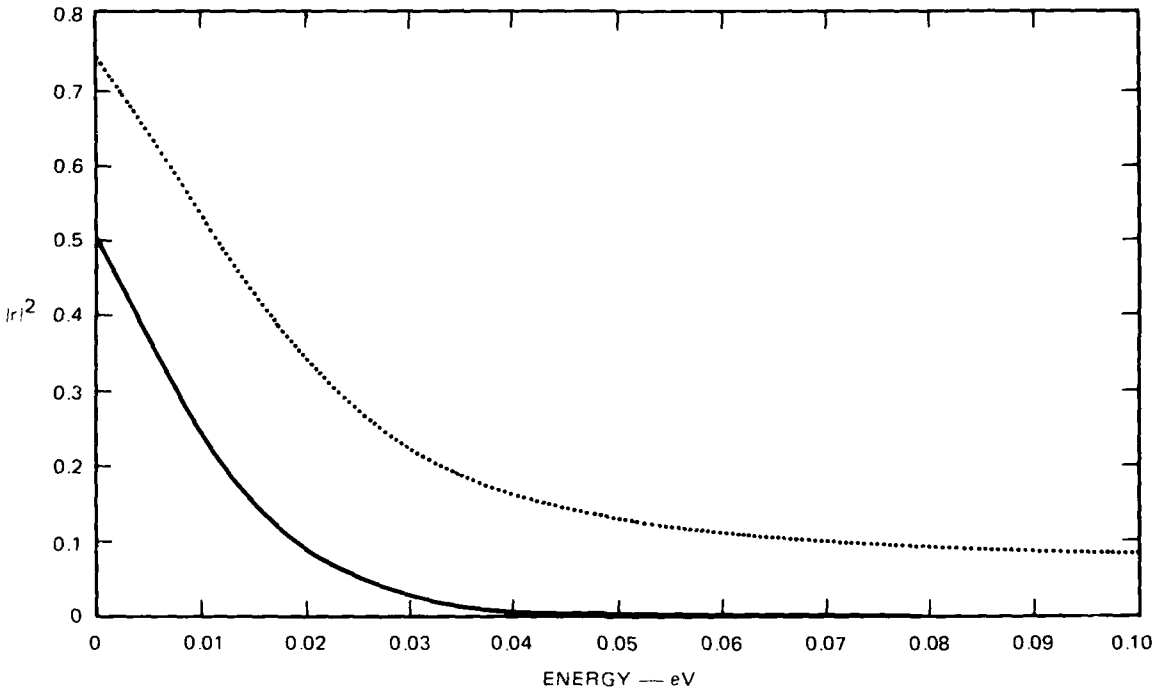


FIGURE 1 REFLECTION PROBABILITY OF AN ELECTRON SCATTERED BY A SCHOTTKY BARRIER

In summary, development of the tools required for a quantitative study is proceeding on schedule. Within the next few months, we expect to be able to assemble the pieces to make careful studies of at least some aspects of transport through a Schottky barriers. Eventually it is expected that the Schottky barriers work also will evolve into an effective modeling tool for the study of junctions and high-speed electronics devices.

The next section presents a draft of a paper in preparation on the electrostatic potential from dopants in the depletion region. As mentioned previously, the resulting barrier is shown to be remarkably similar to the quadratic potential of a jellium, as is usually assumed. The difference between these potentials acts as a perturbation to electrons traversing the barrier; it is shown to be small and the scattering weak.

II EFFECT OF DISCRETE DOPANTS IN SCHOTTKY BARRIERS

Traditionally the barrier in Schottky barriers and heterojunctions is modeled by a one-dimensional quadratic potential, as would obtain from jellium of charge in the depletion region. Fluctuations in the potential act as a perturbation to electrons traversing the barrier; particularly important are the fluctuations in the plane normal to the barrier.

At first glance it might seem that the difference in electrostatic potential from a random distribution of ionized dopants and a jellium is large and that it would strongly scatter electrons traversing the depletion region. Boudville and McGill (1985) calculated transport using a simple model for the coulomb potential and found the effect to be large. This section presents a more complete study of this perturbation. We do so with an approximate potential and later show the results of a more complete Madelung calculation using a collection of 100 randomly distributed dopants.

To make an approximate perturbation to the true potential, consider a single sphere of radius r_s and volume $1/N_d$, where N_d is the dopant density. The charge density inside the sphere is made out of a point charge at the center, compensated by uniform background of density N_d. The potential from all dopants is obtained from a superposition of these sphere potentials; this deviates from the true perturbation because the charge density is doubly counted in regions of overlapping spheres and not counted in void regions. The net charge of both the true and approximate perturbations is zero. (There is an additional approximation of the same order, that the potential from the superposition of charge densities is taken to be equal to the superposition of potentials from the densities separately—a correction comes from the regions where the densities overlap.) This approximation essentially the same as the atomic spheres approximation in electronic structure calculations. For close packed lattices, it is an excellent one, introducing errors of few percent. For a random distribution of dopants, the approximation should still be reasonable. The potential for a single sphere is, in atomic Rydberg units:

$$\phi(r) = \frac{2}{r} + \frac{r^2 - 3r_s^2}{r_s^3} \quad , \tag{1}$$

for $r < r_s$ and zero otherwise. (The potential must also be reduced by the dielectric constant; this reduction will be implicit in all expressions for the potential presented in this paper.)

The average perturbation,

$$\bar{\phi} = N_d \int_{\text{sphere}} d^3r\phi(r) = \frac{3}{5r_s} = \frac{3}{5}\left[4\frac{\pi}{3}N_d\right]^{1/3} \quad , \tag{2}$$

increases as $N_d^{1/3}$, much as the image-force correction, varying as $N_d^{1/4}$. This approximate $\bar{\phi}$ is independent of the distribution of dopants. Its magnitude is small and suggests that the perturbation is weak. For example, for $N_d = 8 \times 10^{18}$ cm^{-3} and $\varepsilon = 10$, $\bar{\phi} \approx 15$ meV, barely observable even by the best IV measurements (appearing a correction to the barrier height) and small compared to the image-force lowering potential.

Now consider scattering by this potential when dopants are ordered on a lattice. For any lattice it is of course possible to obtain the potential by Ewald summation, but our approximate potential should be a quite adequate. When there is a lattice, the perturbation is most informatively expressed as a Fourier series, since the Fourier components are the "oscillator strengths," a measuring of the coupling strength of one state to another, and thus the scattering rate between states. Components of the approximate perturbation are $\phi(G)$ with

$$\sum_{\vec{R}} \phi(\vec{r} + \vec{R}) = N_d \sum_{\vec{G}} \phi(G) \exp i\vec{G} \cdot \vec{r} \quad . \tag{3}$$

Here $\vec{R}$ and $\vec{G}$ are real- and reciprocal-space lattice vectors, respectively, and $\hat{\phi}(q)$ is the Fourier transform of $\phi(r)$,

$$N_d\hat{\phi}(q) = \frac{3}{5r_s} \times \frac{10}{(qr_s)^5}\left[(qr_s)^3 + 3qr_s\cos(qr_s) - 3\sin(qr_s)\right] \quad . \tag{4}$$

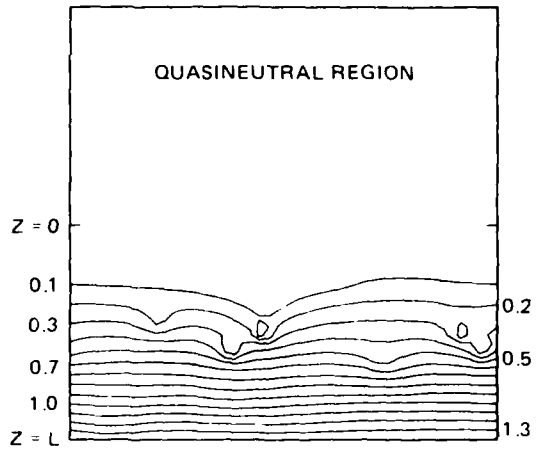
Function $N_d\hat{\phi}(q)$ falls smoothly to zero from its maximum value of $3/5r_s$ at $q = 0$, with a half-width at $qr_s \approx 5$. Again, the strength of the perturbation is small (being strongest at $q = 0$), although in the highly doped case not negligible in comparison to kT. The half-width $qr_s \approx 5$ is a measure of the maximum of change in wave vector $\vec{q}$ an electron will suffer when it

scatters. For example, in the case $m^* = 0.1$ m, $N_d = 8 \times 10^{18}$ cm^{-3} and $\varepsilon = 10$, the "oscillator strength" is 15 meV at $q = 0$ and $\hbar^2(5/R)^2/2m^*$ 35 meV, so that scattering events are limited to a change in energy of approximately 35 meV.

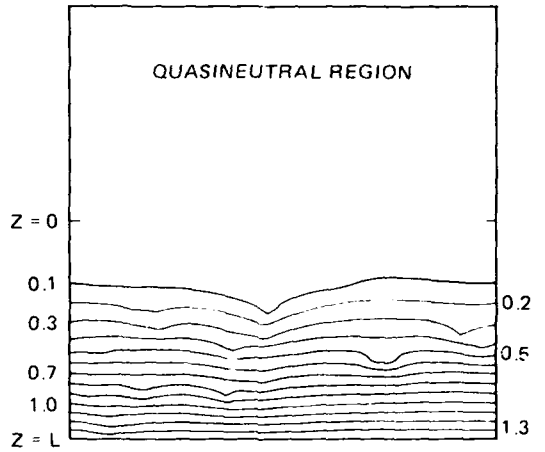
In the case of a random distribution of dopants, the same gross behavior should be found as before; in particular, according to the approximations discussed above, the average perturbation $\overline{\phi}$ is independent of dopant distribution. One might expect that the random distribution will enhance fluctuations, because two or more dopants may cluster together and combine to form a local potential well that strongly influences scattering. As a check of the simple model potential described above, and also to study the effect of randomness, a "sample" depletion region was made out of 100 randomly distributed dopants. The dopants were placed randomly in the bottom half of a supercell of width w and length 2L; the top half contained no dopants and thus constituted a neutral region. Periodic boundary conditions were imposed so that the supercell repeated itself throughout space. The electrostatic potential from this distribution was obtained by Ewald summation, tabulated on a mesh of $50 \times 50 \times 50$ points. A dopant density $N_d = (100 \text{ au})^{-3} \approx 8 \times 10^{18}$ cm^{-3} and a length L = 332 au was chosen, making a barrier height of 1.39 Ryd and a width of w = 548 au. (For $\varepsilon = 12$, this corresponds to about 1.5 eV.)

In the illustrations shown, the z axis is normal to the depletion region. Figure 2 shows contour plots in the yz plane for three different averages of the potential in x. In Figure 2(a), the contours are shown for the 25th plane x, in Figure 2(b), the contours are averaged in x between the 21st and 30th plane, and in Figure 2(c), the contours are averaged in all 50 planes of x. As expected, the potential increases approximately parabolically in the depletion region (between $z = 0$ and $z = L$), and the fluctuations die down as more planes are averaged. Figure 2(a) is not very meaningful because electrons of wave vector k_x will be smeared out in x with a wavelength $2\pi/k_x$. The 10 atomic layers of Figure 2(b) amount to about 50 Å, which corresponds to a transverse kinetic energy of 15 meV for $m^*/m = 0.1$. Figure 2(c) is hardly distinguishable from a parabolic barrier and the barrier height is very close to the value of 1.39 Ryd that a jellium would have.

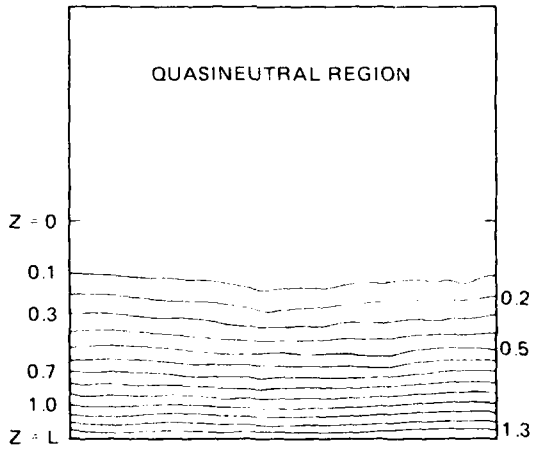
Figure 3 shows the deviation from a jellium, averaged in 10 and 50 planes in x. The 10-plane average is seen to be about three times stronger than the 50-plane average. Figure 3(c) shows the deviation in potential averaged in both x and y. It is seen to rise smoothly from approximately zero near the edge of the depletion region. The average potential in the depletion region can visually be seen to be close to 10 mRy the approximate potential estimates. Figure 4 shows the Fourier transform of the potential in the xy plane, for z in at the edge of



(a) CONTOURS IN THE yz, TAKEN FOR A SINGLE PLANE IN x

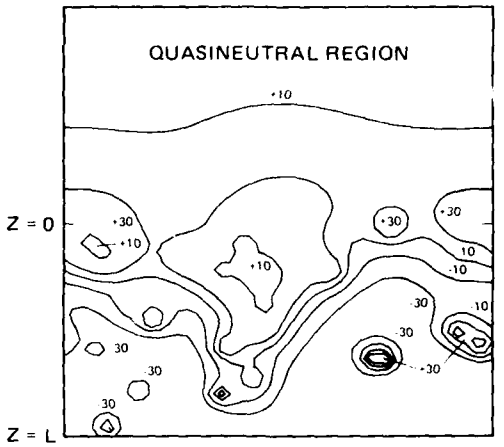


(b) CONTOURS IN THE yz, AVERAGED IN 10 PLANES IN x

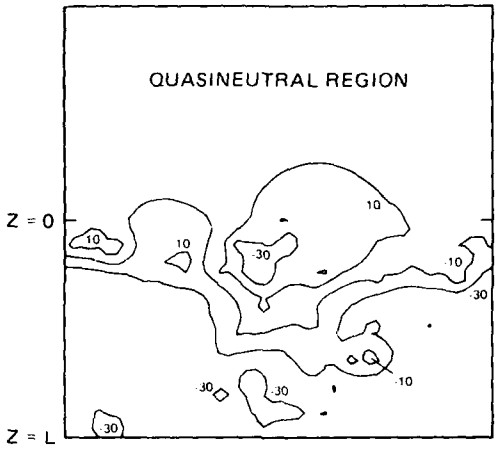


(c) CONTOURS IN THE yz, AVERAGED IN ALL 50 PLANES IN x

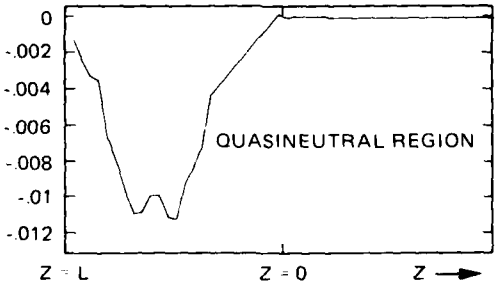
FIGURE 2 CONTOUR PLOT OF A SCHOTTKY BARRIER: CONTOURS OF CONSTANT BARRIER HEIGHT FOR THREE DIFFERENT AVERAGES OF THE BARRIER IN x



(a) CONTOURS OF CONSTANT DIFFERENCE, ANALOGOUS TO FIGURE 2(a)



(b) ANALOGOUS TO FIGURE 2(c)



(c) DIFFERENCE WHEN THE POTENTIAL IS AVERAGED IN THE ENTIRE PLANE NORMAL TO THE SCHOTTKY BARRIERS

FIGURE 3 DIFFERENCE IN POTENTIAL BETWEEN THE JELLIUM AND THE RANDOM DISTRIBUTION OF DOPANTS

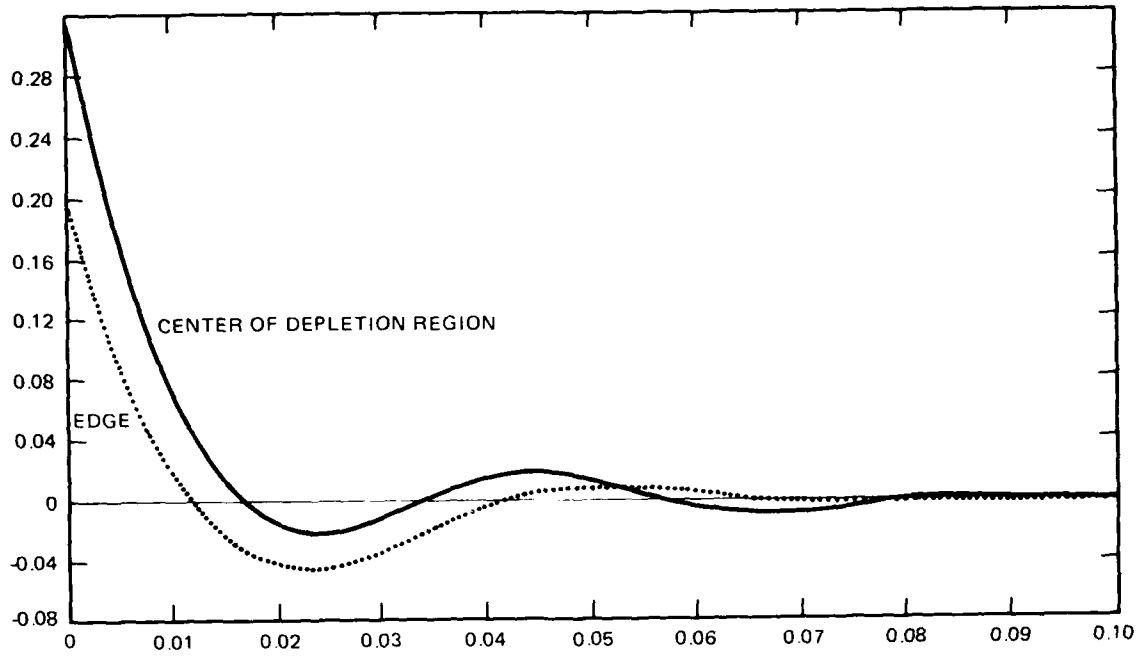


FIGURE 4 FOURIER TRANSFORM OF THE SCHOTTKY BARRIER POTENTIAL AT THE EDGE OF THE DEPLETION REGION

Units of k are 50/w, where w = 548 au.

the depletion region and in the center. The Fourier transform $\hat{\phi}(q_t)$ dies out very rapidly away from $q_t = 0$, indeed too rapidly to be resolved on the discrete mesh used. This rapid decay is perhaps most easily interpreted from the point of view of the model potential. Taking its Fourier transform over a random distribution of dopants,

$$N_d \int d^3r e^{i\vec{q}\cdot\vec{r}} \sum_{\vec{R}} \phi(\vec{r}+\vec{R}) = N_d \hat{\phi}(q) \sum_{\vec{R}} e^{i\vec{q}\cdot\vec{R}} \quad , \tag{5}$$

the sum over a distribution of phases $\vec{q}\cdot\vec{R}$ now washes out all of the Fourier components of this approximate perturbation except for $q = 0$.

Thus, it appears that a random distribution of dopants scatters even more weakly than an ordered lattice. The potential in either case appears to electrons transversing the depletion region to be remarkably like a simple quadratic potential. The key to this perhaps surprising result lies in the long range of the coulomb potential: a superposition of potentials falling off as

1/r combine to form a very smooth potential. (The singularity in a 1/r behavior at short range is not significant, because it is only $\int(1/r)d^3r$ over some volume characteristic of the size of an electron wavelength that matters.) No explicit calculations of scattering through the depletion region were carried out here, although this is rather easy to do. It is clear from the discussion, however, that the net scattering from these dopants are quite small (especially in the more physically significant random case), particularly when averaged over a distribution of electrons. Such a conclusion is the opposite of the conclusion Boudville and McGill (1985) drew. He did carry out transport calculations, but used a crude potential in which only a single dopant was present, and it is probably in the differing treatment of the potential that our conclusions differ.

III AB INITIO ELECTRONIC STRUCTURE WORK

Most properties of interest in the solid are governed by the behavior of the electrons, and these properties can (in principle) be calculated if the underlying Schrödinger equation (or the relativistic extensions to it) could be solved. In particular, the heat of formation of metal adatoms on the surface of semiconductors, the interfacial dipole that pins most Schottky barriers, and of course the energy bands are the kinds of quantities of particular relevance to Schottky barriers. The greatest portion of our efforts in the past year have been devoted towards development of an efficient method for making such electronic structure calculations, one that is sufficiently fast that it can be applied to large systems (by *ab initio* standards) containing several dozens of atoms.

While it is nearly impossible to solve that equation exactly for a real system, the local-density approximation to it has been found to yield remarkably good results under a wide variety of circumstances. Hohenberg and Kohn proved long ago that the Schrödinger equation is a functional only of the electron density; the functional, however, is unknown. The local-density approximation is a simplification of the unknown density functional, and it is possible (although difficult) to make systematic corrections to it. It is *ab initio*, in the sense that no adjustable or empirical parameters enter into the theory. Extensive experience in a truly remarkable range of applications has generated a high degree of confidence in the LDA, and it is widely believed that the it is sufficiently accurate to predict a broad range of properties, particularly mechanical properties. It can be equally well applied to any element in the periodic table and to any arbitrarily complicated system, barring formidable difficulties in accurately obtaining solutions to the LDA for large systems.

Its greatest drawback is that, at least as traditionally applied, it is quite complicated. First a basis set must be chosen in which matrix elements of the Hamiltonian can be calculated. Then the eigenvalue problem must be solved to generate a sum of one-electron energies and a charge density; next, Poisson's equation must be solved to evaluate the Hartree potential and the electrostatic energy. Finally, the total energy is obtained from the eigenvalue sum, plus a double counting correction in the Hartree potential. *Ab initio* methods, as least in their traditional application, additionally require self-consistency in the potential, i.e., the potential as

calculated from the eigenstates of the Hamiltonian must be identical to the potential that generated the Hamiltonian in the first place. Until recently as last year, the available computational techniques were still regarded as far too cumbersome to calculate properties of anything but very small systems, e.g., systems with 20 atoms or less. The bulk of our effort this year has gone into development of an efficient method that solve the local density equations far more efficiently than previously. This opens many doors that were previously closed to *ab initio* calculations; in particular, it should be possible to make *ab initio* studies of the metal-semiconductor interface.

An accurate solution of the local density-functional is a complex and computationally intensive task. This has until now been particularly so with techniques that attempt to solve the local-density equations with essentially no approximations (the APW, LAPW, and pseudopotential methods). Calculations using smaller, more efficient basis sets, in particular the linear muffin tin orbitals (LMTO) method, traditionally make simplifying approximations to the potential. The LMTO method is far more efficient than its sister methods, but the approximations to the potential render it suitable only in conditions of high symmetry.

The bulk of our efforts this year have been spent in collaboration with Dr. Methfessel at the Max Planck Institut für Festkorperforschung in Stuttgart, to develop a new LMTO method that removes the approximations to the potential. Because the method is only now being completed, very few results are available. However, the early results are very promising. The LMTO method, without any shape approximations to the potential, and with an enlargement over the conventional basis can be as accurate as the computationally intensive methods (Methfessel, 1988; Methfessel and van Schilfgaarde, in preparation). Silicon has been used as a testing ground; it makes for a particularly stringent test for the LMTO method because of its open tetrahedral structure (the LMTO method prefers close-packed structures). Table 1 attests to the remarkable precision of both density-functional theory and this new LMTO method.

This basis set of 22 orbitals/atom is sufficient to solve the local-density equations to an absolute precision of about 1 mRy. Comparable accuracy using the pseudopotential method requires about 1000 plane waves per atom (similarly for the LAPW method). Because the computation time for a given calculation of the energy eigenvalues increases as the third power of the number of orbitals in the system, it is obvious that this method is orders of magnitude faster than the pseudopotential method for comparable accuracy. The reason why the LMTO method is so efficient is that its orbitals are tailored to the potential of the system, and so very rapid convergence is obtained.

Table 1

PROPERTIES OF SILICON CALCULATED SELF-CONSISTENTLY FROM 22-ORBITAL BASE, FULL POTENTIAL

Data from Methfessel (in preparation)

Parameter	Experiment	Theory
Lattice constant (a.u.)	10.26	10.23
Cohesive energy (eV)*	4.8	5.23
Bulk modulus (Mbar)	0.98	0.987
$c_{11} - c_{12}$ (Mbar)	1.02	1.03
c_{44} (Mbar)	0.80	0.83
Phonons:		
TO(Γ) (THz)	15.53	15.52
Kxyz (eV/Å)	−35.1	39.1
TO(X) (THz)	13.90	13.75
LAO(X) (THz)	12.32	11.82
TA(X) (THz)	4.49	4.50
Grüneisen parameters:		
TO(Γ)	0.98	
TO(X)	1.5	1.51
LAO(X)	0.9†	1.03
TA(X)	1.4	1.42

*This is essentially the result of local-density theory, and the error is almost entire owing to failure of the local density in the free atom, as opposed to the solid.

†There is a large uncertainty in the measurement of this quantity (Manuel Cardona, private communication).

LMTO calculations have been performed on large systems, including the $NiSi_2$-Si interface, using nine interfacial layers comprising 80 atoms (Das et al., submitted; Das et al., in press) and one on a 216-atom silicon cluster thought to resemble amorphous silicon. This demonstrates the feasibility of applying the LMTO method to large systems; our present task is to do the same with the accurate, full-potential version of the LMTO method.

Another theoretical development important to *ab initio* treatment of large systems comes in new approaches to the density-functional. Self-consistency can be a real obstacle in conventional applications, first because it is slow, and secondly because it is hard to reach, owing to the many more degrees of freedom. A recent development by Car and Parrinello unites density-functional theory and molecular dynamics, and self-consistency in the electronic structure is achieved simultaneously with the motion of the nuclei (Car and Parrinello, 1985). This has been successfully applied to a (001) twist boundary in germanium, using the pseudopotential method a local approximation to the exact LDA pseudopotential (Payne, Bristowe, and Joannopoulos, 1985).

Another recently developed technique (Harris, 1985; Foulkes, 1987) is even simpler than the above mentioned Car and Parrinello method, and more efficient for the LMTO method. These techniques are derivatives of a method originally published by Harris (1985), and independently and more completely by Foulkes (1987). The essential point here is to exploit the variational property of the Hamiltonian, because of which errors in the total energy are second order in the difference between the guessed input potential and the self-consistent potential. Rather than carrying calculations to self-consistency, one attempts to construct an input potential sufficiently close the the self-consistent one as to render unnecessary any steps to self-consistency. Another key in this technique is that the density-functional can be written in another form so as to require only a guessed input potential and the output band structure energy.

The Hohenberg-Kohn density functional at a density n is

$$E[n] = T[n] + E_{Hartree}[n] + E_{xc}[n] + \int nV_{en}[n] \quad ,$$

where $E_{Hartree}[n]$ is the electrostatic energy $1/2\int n(r)\, n(r')/|r - r'|d^3rd^3r'$ of the electrons, $\int nV_{en}$ is the energy of the electrons interacting with the nuclei and $E_{xc}[n]$ is the exchange-correlation energy.

The kinetic energy T is not directly calculable, but it can be obtained by solving the Schröinger equation for its eigenstates ψ_i and eigenvalues ϵ_i:

$$(T + v_{in})\, \psi_i = \epsilon_i \psi_i \quad ,$$

where $T = -1/2\nabla^2$ and v_{in} is a guessed input potential. Solution of the one-electron equations for ψ_i yields an output charge density

$$n_{out} = \sum_i \psi_i^* \psi_i \quad ,$$

where $\sum_i$ is the sum over occupied orbitals. Were v_{in} the self-consistent potential, n_{out} would be the self-consistent density n_0 as well, and v_{in} would then be

$$v_{in} = V_{en}(r)[n_0] + \int \frac{n_0(r')}{|r - r'|} d^3r' + \mu_{xc}[n_0] \quad ,$$

but (and this is the central point of this approach) v_{in} need not be calculated from any density (Foulkes, 1984).* Because of the variational principle, any guessed input potential incurs errors of order $(n_{out} - n_0)^2$. Solution of the above equations yields an expression for the kinetic energy:

$$T[n_{out}] = \sum_i \int \psi_i^* T\psi_i = \sum_i \varepsilon_i - \int v_{in} n_{out} \quad .$$

Making a functional Taylor series in T,

$$T[n_{in}] = T[n_{out}] + \int (n_{in} - n_{out})(\delta T/\delta n_{in}) + O(n_{in} - n_{out})^2 \quad ,$$

and using $\delta T/\delta n_{in} = -v_{in}$ + constant, Foulkes (1987) obtained a new expression for the total energy

$$\tilde{E}[n_{in}, v_{in}] = \sum_i \varepsilon_i + \int (V_{en} - v_{in}) n_{in}$$

$$+ E_{Hartree}[n_{in}] + E_{xc}[n_{in}] + O(n_{out} - n_{in})^2 + O(n_{out} - n_0)^2 \quad .$$

This last expression differs from the self-consistent one by errors of second order in the density. It is exactly equivalent to the density-functional as originally formulated, but is amenable to approximation, especially with respect to the LMTO method. In particular, the LMTO

*The idea that the input potential v need not be derived from an input density, also due to Foulkes, is recent and is as yet unpublished.

method considerably simplifies if it is sufficient to construct a starting potential from a superposition of spherical atom-centered potentials. M. Methfessel (in preparation) has constructed a test potential in silicon and found good agreement with the fully self-consistent results. Importantly, the same test potential can be put in different structures (e.g., beta-tin, diamond, simple cubic), so it is transferable to new environments. Self-consistency is thus obviated. This method is in practice essentially as efficient than the semiempirical tight-binding method, but has the full support and precision of density-functional theory. Indeed it very strongly resembles the tight-binding method since essentially all that enters are the sum of one-electron energies. One of the greatest achievements of the Harris functional is to make a formal justification of most of the ansatz used implicitly in semiempirical tight-binding methods. The method outlined here is far more efficient than the Car-Parrinello method and is well suited for large systems.

A related approach is to make a guessed potential out of a superposition of free-atomic charge densities. This is more complicated to implement since the potential is no longer a superposition of spherical potentials, but the results seem about as good (Polatoglou and Methfessel, 1988) except for very ionic systems such as NaCl.

IV SUMMARY AND FUTURE WORK

One step in the current suite of LMTO programs involves a technique that solves Poisson's equation and the exchange-correlation potential and energy in the interstitial (Methfessel, 1988; Methfessel and van Schilfgaarde, in preparation). The idea is to fit the density as evaluated at the surfaces of the spheres to a linear combination of spherical Hankel functions; since Hankel functions are eigenfunctions of the Poisson equation, the Hartree potential is trivially obtained as a linear combination of Hankel functions once the fit to the density is known. While ingenious, the method as originally designed was not suitable for large systems because of the method used to fit the density itself. However, we have recently shown (Methfessel and van Schilfgaarde, in preparation) that procedure is mathematically equivalent to a generalization of Andersen's tight-binding transformation (Andersen, 1985), and that the procedure can be made far more efficient than previously. In particular, it is possible to solve Poisson's equation in real space; the method is equally well suited to molecules. It was principally in this step that the method as originally implemented was not suitable for large systems; this difficulty is being removed with the current work.

A number of improvements need be made to make it fully operational, for example, the full-potential version of the code is as yet neither relativistic nor spin polarized. Without the atomic spheres approximation (in which the potential is constructed out of large overlapping spheres), semicore states are a greater problem than previously and probably a two-panel facility will be required. These are a number of details that need to be filled out for the method to be generally applicable to any system. We believe that this new method shows a great deal of promise and will find wide application in the years to come. Because it is both very accurate and very fast we believe it will ultimately displace all other present-day *ab initio* techniques for calculating electronic structure as the method of choice. For example, it should be possible to study the metal-semiconductor interface, and the role of impurities there and interface states there. With a Cray II, it is possible for the method to perform calculations on several hundreds of atoms.

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This report summarizes the technical progress made in the past year under the auspices of AFOSR Contract F49620-86-K-0018. Substantial progress has been made in two key areas, in the study of perturbations to transport in Schottky barriers, and in development of *ab initio* electronic structure techniques tailored to the study of Schottky barriers.

The objective of the Schottky barrier transport studies is to obtain quantitative modeling of current transport through the depletion region that complements the experimental work of Professor Spicer at Stanford, and of the development of electronic structure techniques to provide a means to study the energetics of formation of Schottky barriers, and other properties related to electronic structure, such as band offsets and band structure. Both projects are heavily computational by nature, and this year's progress was mostly confined to developing the required numerical techniques that will yield the desired results. This report shows that substantial progress has been made in both areas, and that we are nearing completion of working tools that will enable to conduct new studies concerning several different aspects of Schottky barrier phenomena.

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